Arabian Journal of Chemistry (2014) xxx, xxx–xxx

King Saud University

Arabian Journal of Chemistry

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ORIGINAL ARTICLE

# Micellar electrokinetic chromatographic analysis of thorium, uranium, copper, nickel, cobalt and iron in ore and fish samples

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Received 20 August 2013; accepted 10 October 2014

KEYWORDS

Analysis of thorium and uranium;
MEKC;
Bis(salicylaldehyde) ethylenediimine;
CE;
Organic modifiers;
Fish

**Abstract** In this study an MEKC method has been developed and applied for the analysis of thorium and uranium from environmental samples. Copper, nickel, cobalt, and iron present in the matrix were analyzed concurrently. The method is based on pre-capillary chelation of analyte with bis(salicylaldehyde) ethylenediimine ($H_2SA_2en$) chelating agent. The analysis was completed within 4 min with uncoated fused silica capillary under the following optimized conditions: borate buffer 60 mM restraining 13 mM SDS (micellar medium) and 11.5% acetonitrile, pH 8, applied voltage 30 kV. The detection was carried out at 231 nm wavelength. Linear dynamic ranges were within 0.4–100 μg $mL^{-1}$ and limits of detection (LOD) within 0.04–0.08 μg $mL^{-1}$ of each element. The analysis of ore samples indicated thorium and uranium within 561–2501 μg $g^{-1}$ and 25–911 μg $g^{-1}$ with RSD 1.7–3.8% and 1.5–3.9% correspondingly. Thorium and uranium in fish samples were found below detection limit. The results of analysis of thorium, uranium, copper, nickel, cobalt and iron obtained by MEKC were comparable with that of supplier's specifications and AAS.


## 1. Introduction

The interest in the determination of thorium has increased because of its potential use in nuclear reactors as fuel for production of electricity by nuclear power plants. The determination of thorium is important because it is about three times more abundant than uranium. The simple and selective method with short analysis time and broad calibration range could be of value in geological prospecting and exploration of thorium (Barkley et al., 1986; Rao and Nair Biju, 2002). Some of the methods used for measurement of Th and U ranging from classical to modern instrumental analytical techniques include radioactive methods (Santos et al., 2004), flame atomic absorption (Mayer et al., 2001), neutron activation analysis (Byrne and Benedik, 1997), photon electron rejecting alpha liquid scintillation (PERALS) (Dacheux and Aupiais, 1997; Dacheux et al., 2000; Aupiais et al., 2002, 2003), second derivative spectrophotometry (Ramesh et al.,

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Peer review under responsibility of King Saud University.

ELSEVIER Production and hosting by Elsevier

http://dx.doi.org/10.1016/j.arabjc.2014.10.012
1878-5352 

1992), inductively coupled plasma-mass spectrometry (ICP-MS) (Bailey et al., 1993; Agarande et al., 2005), high performance liquid chromatography (HPLC) (Jaison et al., 2006; Raut et al., 2004; Rehkamper, 1995), capillary electrophoresis (CE) (Liu et al., 1998a,b,c; Macka et al., 1998; Mirza et al., 2008a,b, 2009) and CE–ICP-MS (Petit et al., 2010). HPLC separations have been obtained using alpha-hydroxy isobutyric acid as complexing reagent followed by post column reaction with suitable chromogenic reagent e.g. arsenazo-III and 4-(2-pyridylazo) resorcinol (PAR) (Hao et al., 1996; Barkley et al., 1992).

Capillary electrophoresis (CE) has been utilized for the separation of organic and inorganic analytes because of its high efficacy and diversity of separation modes available. It provides short analysis time and requires only small sample volume (10–50 nL) for analysis. A number of groups have indicated CE as a promising technique for the analysis of metal species (Chiari, 1998; Timerbaev, 2000; Timerbaev and Shipgun, 2000; Okada, 1999; Shepherd, 2003; Haddad, 1997). The metal ions have weak UV absorption, thus requiring to complex with a suitable chromogenic reagent. A number of metallochromic ligands have been examined as pre-capillary chelating agents (Macka et al., 1998; Vogt and Klunder, 2001). CE determination of thorium and uranium is based on complexation with arsenazo-III, 2-(2-arsenophenylazo) 1,8-dihydroxyl-7-(4-chloro-2,6-dibromophenylazo) naphthalene-3,6-disulphonic acid or 2-[(2-arsenophenyl)-azo] 1,8-dihydroxy-7-[(2,4,6-tribromophenyl)-azo] naphthalene-3,6-disulphonic acid and cupferron (Liu et al., 1998a,b,c; Chen et al., 1995).

Simple buffers are employed to separate ionic water soluble solutes, but sparingly water soluble samples are addressed by the use of non-aqueous CE, micellar electrokinetic chromatography (MEKC) and micro emulsion electrokinetic chromatography (MEEKC). In MEKC, surfactants are added to the buffer solution to make up critical micelle concentration. The separation principle of MEKC is based on differential partition between the buffered aqueous phase and micellar pseudo stationary phase (Oztekin and Erim, 2000). MEKC has been used by researchers for the separation of metal ions (Kemp, 1998; Takagai and Igagrashi, 2003; Hilder et al., 1998; Isoo and Terabe, 2005; Timerbaev et al., 2002; Haddad et al., 1997; Mirza et al., 2008a,b, 2009).

The chelation and determination of thorium and uranium with ligand *N*,*N*′-ethylene bis(salicylaldimine)[(bis(salicylaldehyde)] ethylenediimine ($H_2SA_2$en) is simple and convenient. $H_2SA_2$en has been extensively studied as a chelating reagent for copper, nickel, palladium, platinum, iron, cobalt, manganese, oxovanadium, oxochromium, dioxomolybdenum and dioxouranium (Floriani and Calderazzo, 1969; Busetto et al., 1973; Gulloti et al., 1977; Pasini et al., 1977; Boreham and Chiswell, 1977; Pasini and Gullotti, 1974; Farmer and Urbach, 1970; Cesarotti et al., 1977; Srinivasan and Kochi, 1985; Hinshaw et al., 1989). Uden and his coworkers used $H_2SA_2$en for HPLC separation and determination of copper, nickel and palladium using normal and reversed phase modes with detection limits in low ng/injection range (Uden and Walters, 1975; Uden et al., 1975). It has also been used for HPLC determination of uranium, nickel, copper and iron in the phosphate rock residues and environmental ore samples (Khuhawar and Lanjwanii, 1996) and uranium from ore samples using MEKC (Mirza et al., 2008a,b). Specificity and selectivity of a chelating reagent for metal ions is of prime importance in CE with pre-column derivatization. The important points required to be considered carefully are: under controlled conditions only a single-state chelate between chelating reagent and an ion should be formed; during electrophoresis in the capillary, the chelate formed should remain un-decomposed; and for the best detection, the $\lambda_{max}$ of the chelates should be close to each other and far-off from that of the chelating reagent (Liu et al., 1998a,b,c). The reagent $H_2SA_2$en can easily be prepared from simple and laboratory chemicals in good yield (90% theoretical). It reacts with limited number of metal ions at all concentrations.

The present work extends the applications of CE for the separation and analysis of thorium and uranium from ore and fish samples using $H_2SA_2$en for the possible use of method for geological prospecting and exploration. The presence of copper, cobalt, nickel and iron in the matrix could also be analyzed concurrently.

## 2. Experimental

### 2.1. Reagents

The reagent $H_2SA_2$en and its cobalt, copper, nickel, iron, thorium and uranyl chelates were prepared as reported (Uden et al., 1975). Guaranteed reagent grade hydrochloric acid (37%), ethylenediamine, acetonitrile, chloroform, ammonium acetate, potassium chloride, acetic acid, sodium acetate, boric acid, sodium tetraborate, sodium bicarbonate, ammonium chloride and ammonia solution (35%) were from E-Merck (Germany), Salicylaldehyde (Fluka, Switzerland) and methanol (RDH, Germany) were used.

Metallic salts such as iron chloride, cobalt nitrate, copper acetate, nickel acetate, palladium chloride (E-Merck, Germany), uranyl nitrate and thorium oxide (BDH, Chemicals Ltd., UK) were used. The ore samples (Sandstone house reference standards) were kindly provided by Atomic Energy Mineral Centre, Lahore, Pakistan.

### 2.2. Preparation of stock solutions

Stock solutions (50 mL) containing 1 mg/mL of Co, Cu, Ni, Fe and U were prepared by dissolving appropriate amounts of metal salts in water. In case of U (VI) and Fe (III)), 0.5 mL of nitric acid (37%) and 0.5 mL of sulphuric acid (98%) were added respectively to prevent hydrolysis before adjusting the volume. Requisite amount of $PdCl_2$ was added to hydrochloric acid (5 mL, 37%) and heated gently till the dissolution of all $PdCl_2$. The solution was concentrated to 0.5 mL and volume was adjusted to 50 mL. The calculated amount of $ThO_2$ was added 10 mL hydrochloric acid (37%) and nitric acid (65%) (3:1 by volume) and heated gently till it dissolved entirely. The solution was concentrated to 1 mL and the volume was adjusted up to the mark. The standard solution of cobalt (III) was prepared as under: cobalt (II) solution (25 mL) containing 1 mg/mL was added 5 mL nitric acid (65%) and the solution was heated to near dryness. Finally, the volume of the solution was adjusted to 25 mL by the addition of double distilled water.

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### 2.3. Preparation of buffers

Buffer solutions at unit intervals (pH 1–10) were prepared from: hydrochloric acid (0.1 mol/L) and potassium chloride (0.1 mol/L) pH 1 and 2; acetic acid (0.1 mol/L) and sodium acetate (0.1 mol/L) pH 3–6; boric acid (0.1 mol/L) and sodium tetraborate (0.1 mol/L) pH 8 and 9, and sodium bicarbonate and sodium carbonate (0.1 mol/L) pH 10.

### 2.4. Equipment and MEKC

The CE was carried out with a Beckman Coulter P/ACE system equipped with auto sampler, MDQ software and photodiode array detector. Uncoated silica capillaries of required length ad internal diameter were obtained from Beckman Instruments. CE was performed at room temperature. Before the start of the analysis, capillary was regenerated and conditioned as shown below:

i. Methanol was run for 1 min.
ii. Washed with water for 30 s.
iii. Hydrochloric acid (0.1 M) was run for 2 min.
iv. Washed with water for 30 s.
v. Solution of sodium hydroxide (0.1 M) was run for 2 min.
vi. Washed with water for 30 s.
vii. Conditioned with back ground electrolyte for 2 min.

To obtain the reproducible results, the capillary was washed with sodium hydroxide (0.1 mol/L) for 1 min., water for 0.5 min and then equilibrated with the back ground electrolyte for 1 min before the injection of each sample. The sample was introduced by an auto sampler with pressure of 0.5 Psi for 5 s. The electrophoretic migration was optimized with boric acid–sodium tetraborate: SDS (3:1 v/v) at final concentrations of 60 mmol/L and 13 mmol/L, respectively with applied voltage 30 kV at pH 8. The power supply was 0.5–0.8 W with current of 34–39 μA. The UV detection was at 231 nm. The electrophoretic mobilities of metal chelates were measured as reported (Mirza et al., 2008a,b).

pH measurements were made with Orion 420-A pH meter (Orion Research Inc., Boston, USA) with combined glass electrode and reference internal electrode. The determination of copper, cobalt, nickel and iron was carried out by Varian Spectra A-20 atomic absorption spectrophotometer with standard burner head and air–acetylene flame at the conditions recommended by the manufacturer. Copper, cobalt, nickel and iron were determined at 324.8 nm, 240.7 nm, 232.0 nm, and 248.3 nm, respectively in quadruplet ($n = 4$).

### 2.5. Pre-capillary derivatization procedure

Aqueous solutions (1–3 mL) containing appropriate quantities within 1–200 μg each of uranium, thorium, iron, nickel, copper and cobalt were transferred to 10 mL sample vials and acetic acid–sodium acetate buffer (pH 6, 2 mL) was added. The reagent solution $H_2SA_2$en (1.5 mL, 1% w/v in ethanol) was then added and contents were heated on water bath at 70 °C for 10 min. After cooling at room temperature, chloroform (2 mL) was added and the contents were mixed well. After separation with a separating funnel, organic layer (1.5 mL) was transferred to the sample vial. The organic layer was evaporated and the residue was dissolved in an optimized solvent system (1.5 mL) comprising methanol: acetonitrile: water (2:2:1 v/v/v). The complex was run through capillary and electropherograms were recorded at the optimized conditions.

### 2.6. Preparation of ore samples

Ore samples containing thorium and uranium were mixed with 15 mL of hydrochloric acid (37%) and 7 mL of nitric acid (65%) and heated quietly on a hot plate until most of the acid evaporated. The samples were heated several times to near dryness after the addition of nitric acid (7 mL). Finally, the residues were dissolved in 0.1 M nitric acid. The solutions were filtered and volume was adjusted up to 15 mL. The solution (3 mL) was taken and pre-capillary derivatization procedure was followed. The quantification was carried out by an external calibration plot prepared from standard solutions using the $y = mx + c$ based linear regression equation.

### 2.7. Analysis of thorium and uranium by standard addition

The sample $TU_6$ (0.3 g) was taken and processed as "Pre-column Derivatization Procedure". Solution (2 mL) in duplicate was taken and one of the portions was added uranium and thorium (50 μg each in aqueous phase) and "Pre-column Derivatization Procedure" was followed for both the portions. The quantification was carried out using linear calibration curve and from an increase in the response with added thorium or uranium.

### 2.8. Analysis of fish for metal ions

For analysis of metal ions, fish (fresh water) weighing 400–500 g were dissected in the lab and 30 g muscle was shifted to a digestion flask fitted with a condenser. Nitric acid (65%) 30 mL, sulphuric acid (98%) 10 mL and ammonium molybdate (2% w/v) 2 mL were added and heated quietly on a hot plate till the appearance of white fumes. Nitric acid (15 mL) was mixed and stuffing was again heated until the formation of a clear solution. The solution was concentrated to about 5 mL, pH was adjusted and the volume was made up to 20 mL. The solution (3 mL) was treated as pre-capillary derivatization procedure. Then, the quantification was carried out by using an external calibration curve constructed from standard solution.

## 3. Results and discussion

The reagent $H_2SA_2$en reacts with cobalt, copper, nickel, iron, palladium, thorium and uranium to form chelates, with enough electrophoretic mobility to travel from un-coated fused silica capillary with borate buffer in the presence of SDS at pH 8 with applied voltage 30 kV.

### 3.1. Optimization of the separation conditions

#### 3.1.1. Background electrolyte, surfactants and organic modifiers

The pH and type of background electrolyte is of prime importance in CE separations/determinations. During this study,

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four different electrolytes sodium acetate–acetic acid, phosphate, carbonate–bicarbonate and boric acid–sodium borate were investigated regarding their impacts on the separation of metal chelates. Among these, boric acid–sodium borate buffer proved better in selectivity, reproducibility and efficacy. Therefore, borate buffer (60 mM) was optimized as running buffer at pH 8.

The reagent $H_2SA_2en$ forms neutral complexes with certain metal ions and the separation is carried out with appropriate surfactants. In this study, different anionic surfactants such as SDS, sodium lauryl ether sulphate (SLES) and perfluorooctane sulphonate (PFOS) were investigated as pseudo stationary phases by varying concentrations of 8–16 mmol/L. A good resolution of peaks for metal contents was observed at 11.5 mmol/L SDS concentration. As a rule of thumb, migration time could be extended by adding appropriate organic modifiers to the running buffers. Therefore, to improve the separation between metal ion complexes, a number of organic modifiers such as acetonitrile, isopropanol, and ethanol were tested. Acetonitrile is less viscous than methanol, allows detection at lower wavelengths and causes fewer fluctuations in pressure. It has better selectivity and forms less bubbles when mixed with water, hence, as an organic modifier, it showed good results on selectivity and separation. It is reported that organic modifiers bring about changes in EOF at the given applied potential in CE (Liu et al., 1998a,b,c). Such changes could be linked to alteration in the viscosity of the buffer or in the zeta-potential developed by electrical double layer of the silica wall. pH and EOF play significant role when anionic surfactants are used for separation of neutral compounds in uncoated fused-silica capillaries. The EOF is sufficiently stronger than the electrophoretic migration at neutral to alkaline pH; hence, almost all micelles are swept towards the cathode. During migration, cations lead the neutrals which are followed by anions. The pH effect of back ground electrolyte on migration time was therefore assayed in the range 7.0–9.0. Acetone was injected as electro osmotic flow marker and the mobility of the metal chelates was determined by using the following equation:

$$\mu = L_t L_d / E[1/t_m - 1/t_o]$$

where $\mu$ is the electrophoretic mobility of analyte ($cm^2\,kV^{-1}\,s^{-1}$), $L_t$ indicates the total length of capillary (cm), $L_d$ denotes the length of the capillary up to the detector (cm), $E$ stands for the applied potential (kV) and migration time of the analyte is $t_m$.

During this study, an attempt was made to reproduce the separation and complete separation was achieved under optimized conditions (Fig. 1). The identification of the peaks was based on migration time determination for the metal chelates separately and confirmed by spiking each metal ion in a sequence in the mixture. The electrophoretic mobilities of the chelates of iron, uranium, thorium, copper, nickel and cobalt at the optimized pH were calculated −15.41, −12.71, −9.66, −7.98, −5.23, −3.61, and 6.96 $cm^2\,kV^{-1}\,min^{-1}$, respectively. The repeatability of the derivatization and separation was examined. The variations in peak height for inter ($n$ = 5) and intra ($n$ = 5) day were observed with relative standard deviation (RSD) 2.3–3.7% and 2.2–3.1% and migration time 1.2–1.7% and 1.1–1.5%, respectively.

Fresh calibration curves were constructed for each metal ion with standard metal ion solutions, following the analytical procedure, followed by sample analysis (Table 1). The analysis of test solutions of thorium and uranium ($n$ = 5) to cover the calibration range indicated relative error within ±2.5% and 2.9%, respectively. During the investigation of the interfering effect under optimized conditions, Mn (II), Zn (II) and Cr (III) when added in concentrations as that of Th (IV) and U (VI) did not interfere. The presence of Al (III) decreased the % extraction of Th and U, but was masked with (1 mL, 1% w/v) $NH_4F$ and relative % error was within ±1.8%.

### 3.2. Application of the proposed method

#### 3.2.1. Analysis of thorium and uranium from ore samples

To assess the quantitative applicability of the developed procedure, six ore samples containing thorium and uranium

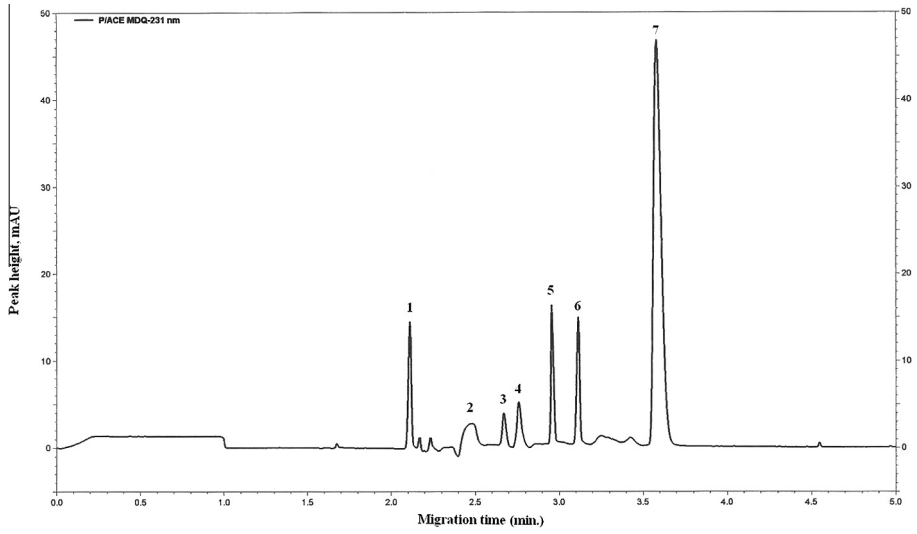


**Figure 1** Separation and analysis of Co (1), reagent $H_2SA_2en$ (2), Ni (3), Cu (4), Th (5), $UO_2$ (6), and Fe (7) by use of un-coated fused silica capillary with 75 μm id at 25 °C, 11.5 mM SDS, 60 mM borate buffer, pH 8, voltage 30 kV and UV detection at 231 nm.

**Table 1** Quantitative data for MEKC of metal chelates of $H_2SA_2en$.

| Metal ions | Calibration range (μg mL$^{-1}$) | Limit of detection (LOD) (μg mL$^{-1}$) | Coefficient of determination |
|---|---|---|---|
| Uranium | 0.80–100 | 0.08 | 0.9991 |
| Thorium | 0.40–100 | 0.04 | 0.9992 |
| Iron | 0.50–100 | 0.04 | 0.9993 |
| Nickel | 0.80–100 | 0.08 | 0.9991 |
| Copper | 0.80–100 | 0.08 | 0.9995 |
| Cobalt | 0.50–100 | 0.04 | 0.9988 |

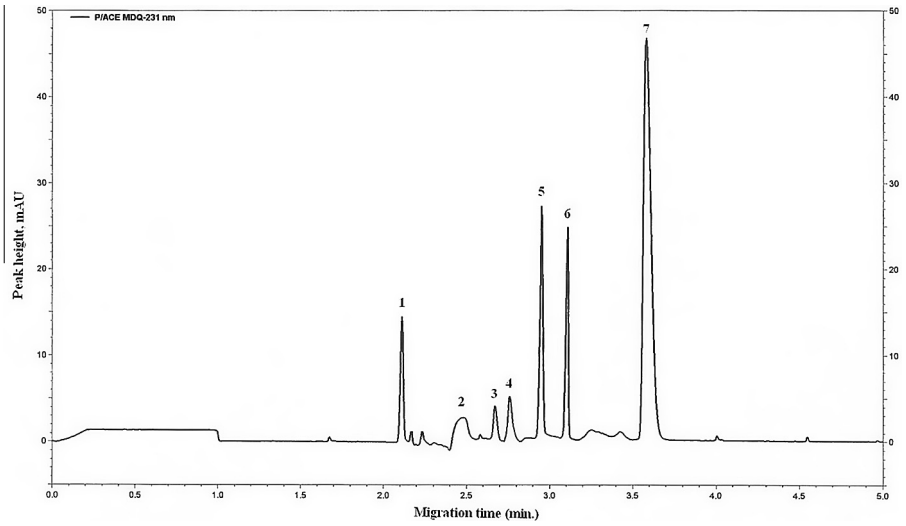


**Figure 2** Analysis of ore sample spiked with thorium and uranium (50 μg each). Conditions as in Fig. 1.

**Table 2** Quantitative analysis of uranium, thorium, iron, nickel, copper and cobalt as chelates of $H_2SA_2en$ in ore samples (μg/g).

| Sample No. | Amount of uranium reported by supplier | Amount of uranium found by CE (RSD %) | Amount of thorium reported by supplier | Amount of thorium found by CE (RSD %) | Metal ions | Amount found by CE (RSD %) | Amount found by AAS (RSD %) |
|---|---|---|---|---|---|---|---|
| TU1 | 785 | 801 (2.5) | 1480 | 1439 (2.1) | Fe | 50277 (1.9) | 50950 (2.8) |
| | | | | | Ni | 19.1 (1.4) | 18.5 (1.7) |
| | | | | | Cu | 30.3 (3.6) | 31.1 (4.3) |
| | | | | | Co | 12.2 (2.3) | 11.6 (2.9) |
| TU2 | 882 | 911 (3.2) | 2450 | 2501 (1.7) | Fe | 44998 (2.3) | 45558 (3.9) |
| | | | | | Ni | 14.5 (2.9) | 15.2 (3.8) |
| | | | | | Cu | 16.6 (2.7) | 15.5 (3.8) |
| | | | | | Co | 26.8 (3.2) | 27.4 (3.6) |
| TU3 | 189 | 183 (1.5) | 1300 | 1335 (2.6) | Fe | 51318 (1.6) | 51833 (2.8) |
| | | | | | Ni | 14.9 (2.1) | 14.3 (3.5) |
| | | | | | Cu | 103.2 (1.7) | 104.4 (3.3) |
| | | | | | Co | 19.3 (1.3) | 18.7 (2.4) |
| TU4 | 86 | 90 (2.7) | 1120 | 1153 (3.2) | Fe | 36122 (2.3) | 36633 (3.9) |
| | | | | | Ni | 18.6 (2.2) | 19.2 (3.6) |
| | | | | | Cu | 135.2 (2.6) | 131.1 (3.4) |
| | | | | | Co | 12.9 (3.7) | 13.5 (3.9) |
| TU5 | 23.7 | 25 (3.9) | 877 | 835 (3.5) | Fe | 51487 (1.5) | 50950 (3.1) |
| | | | | | Ni | 1.9 (3.1) | 2.1 (2.9) |
| | | | | | Cu | 330.1 (1.6) | 334.8 (2.7) |
| | | | | | Co | 14.6 (2.8) | 15.3 (3.6) |
| *TU6 | 72 | 75 (3.4)<br>*70.9 (3.1) | 542 | 561 (3.8)<br>*525 (2.3) | Fe | 57416 (2.7) | 56942 (3.2) |
| | | | | | Ni | 14.8 (1.8) | 14.2 (4.1) |
| | | | | | Cu | 19.3 (2.9) | 18.9 (4.1) |
| | | | | | Co | 153.7 (3.5) | 155.5 (4.2) |

* Sample analyzed by standard addition technique for Th and U.

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**Table 3** Results from analysis of metal ions in fish samples (μg/g).

| Fish | U found by CE (RSD %) | Th found by CE (RSD %) | Fe found by CE (RSD %) [found by AAS] | Ni found by CE (RSD %) [found by AAS] | Cu found by CE (RSD %) [found by AAS] | Co found by CE (RSD %) [found by AAS] |
|---|---|---|---|---|---|---|
| Mystus seenghala (Singhari) | ND | ND | 219 (1.8) [220 (1.9)] | 91 (1.6) [95 (1.9)] | 76 (3.1) [73 (2.1)] | 311 (2.1) [314 (1.8)] |
| Rita rita (Khago) | ND | ND | 329 (2.1) [320 (1.5)] | 108 (1.5) [110 (1.8)] | 98 (2.2) [96 (1.8)] | 213 (1.8) [210 (2.2)] |
| Catla catla (Thaila) | ND | ND | 371 (1.9) [367 (2.2)] | 99 (2.6) [101 (1.7)] | 103 (1.6) [105 (2.1)] | 119 (1.9) [116 (1.6)] |

ND = not detected.

**Table 4** Comparison of the detection limits and separation times of reported methods.

| Ref. | Background electrolyte | Complexing ligand | LOD Th, U ($\mu g\ mL^{-1}$) | Separation time |
|---|---|---|---|---|
| Liu et al. (1998a,b,c) | 30 mM NaAc–HCl buffer containing 0.5 mM cetyltrimethylammonium bromide and 0.2 mM chelating reagent, pH 4.30 | 2-[(2-Arsenophenyl)azo]-1,8-dihydroxy-7-[(2,4,6-tribromophenyl)azo]naphthalene-3,6-disulphonic acid | 0.037, 0.039 | < 4 min |
| Liu et al. (1998a,b,c) | $20 \times 10^{-3}$ mol $L^{-1}$ NaAc–HCl | 2-(2-Arsenophenylazo)-1,8-dihydroxy-7-(4-chloro-2,6-dibromophenylazo)naphthalene-3,6-disulphonic acid | 0.017, 0.141 | 10 min |
| Mallah et al. (2010) | 64 mM borate, 12.25 mM SDS, 13% acetonitrile | Bis(acetylacetone)ethylenediamine (H2AA2en) | 0.11, 0.22 | < 5 min |
| Öztekin and Erim (2000) | 15 mmol HIBA, 13 mM Tris pH 4.9 | Cupferron | 0.24, 0.47 | 7 min |
| Macka et al. (1998) | 15 mM citrate pH 4.7 | Arsenazo (III) | 0.06 $UO_2$ | 3.5 min |
| Present study | Borate buffer 60 mM, SDS (micellar medium) 11. 5 mM, acetonitrile 12%, pH 8 | Bis(salicylaldehyde) ethylenediimine ($H_2SA_2en$) | 0.037, 0.079 | < 4 min |

were analyzed for simultaneous determinations. The amounts of thorium and uranium found were observed within 561–2501 μg/g and 25–911 μg/g with RSD 1.7–3.8% and 1.5–3.9% for Th and U, respectively. A sample ($TU_6$) was spiked with Th and U and the results of analysis indicated recovery as 96.9% and 98.5% with RSD 2.3% and 3.1%, respectively (Fig. 2) (Table 2). The samples also contained Fe, Ni, Cu and Co and were determined simultaneously with RSD within 1.3–4.3% and the results obtained were compared with flame AAS and good agreements with no significant difference at 95% confidence level were observed for all the analyzed elements (Table 2).

### 3.2.2. Fish analysis

The method was also applied for analysis of separated metal ions in fish. Thorium and uranium were found below detection limit. The results of iron, copper, nickel and cobalt found by CE and AAS are listed in Table 3.

### 3.3. Comparison of the developed method

Thorium and uranium could be separated by a number of methods but the use of MEKC is not frequent. Different methods regarding the separation and determination of thorium and uranium have been compared in Table 4. The table portrays that the LOD and separation time for thorium and uranium are comparable with those of other procedures.

## 4. Conclusion

A simple, rapid and reproducible micellar electrokinetic chromatographic procedure is proposed for the analysis of thorium and uranium in a combined matrix of iron, nickel, copper and cobalt with separation time < 4 min by chelation with $H_2SA_2en$. By using this method perilous extraction steps can be evaded because the chelates of $H_2SA_2en$ with separated metal ions are stable and soluble in the background electrolyte used. The analysis of uranium and thorium in reference ore standards shows that the proposed procedure could be applied to real environmental samples consistently.

## Acknowledgement

The authors like to acknowledge the Director, Atomic Energy Mineral Centre, Lahore, Pakistan for providing 6 house reference standards of thorium and uranium for use in the development of MEKC procedure.

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Please cite this article in press as: Aslam Mirza, M. et al., Micellar electrokinetic chromatographic analysis of thorium, uranium, copper, nickel, cobalt and iron in ore and fish samples. Arabian Journal of Chemistry (2014), http://dx.doi.org/10.1016/j.arabjc.2014.10.012

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